Experimental evidence of anapolar moments in the antiferromagnetic insulating phase of V_2O_3 obtained from x-ray resonant Bragg diffraction

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Abstract

We have investigated the antiferromagnetic insulating phase of the Mott-Hubbard insulator V_2O_3 by resonant x-ray Bragg diffraction at the vanadium K-edge. Combining the information obtained from azimuthal angle scans, linear incoming polarization scans and by fitting collected data to the scattering amplitude derived from the established chemical I2/a and magnetic space groups we provide evidence of the ordering motif of anapolar moments (which results from parity violation coupling to an electromagnetic field). Experimental data (azimuthal dependence and polarization analysis) collected at space-group forbidden Bragg reflections are successfully accounted within our model in terms of vanadium magnetoelectric multipoles. We demonstrate that resonant x-ray diffraction intensities in all space-group forbidden Bragg reflections of the kind $(hkl)_m$ with odd h are produced by an E1-E2 event. The determined tensorial parameters offer a test for ab-initio calculations in this material, that can lead to a deeper and more quantitative understanding of the physical properties of V_2O_3.

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In the case of ions located in crystal positions that are not a center of inversion symmetry, hybridization will occur between the valence orbitals of that ion, thus enabling the possibility of observing electronic transitions to the hybridized states via the mixed dipole-quadrupole (E1-E2) channel in resonant x-ray scattering [1, 2], which is sensitive to the ordering of parity-breaking tensorial moments. For example, the ordering of magnetoelectric toroidal moments (anapoles) might be observed. An anapole moment characterizes a system that does not transform into itself under space inversion. These toroidal moments were initially considered in the context of multipolar expansions in nuclear physics [3] and are related to a distribution of magnetic fields which is quite different from those produced by parity-even multipoles, such as dipole or quadrupole moments. The magnetic field distribution of an anapole looks like the magnetic field created by a current flowing in a toroidal winding, and the field is completely confined inside the winding. Parity-breaking E1-E2 contributions [4] to scattering can be expressed in terms of polar and magnetoelectric tensors that contain the anapole operator [1]. The study of these contributions to resonant x-ray diffraction is of fundamental importance in current developments of the electronic structure of materials with complex electronic properties, such as magnetoelectricity, piezoelectricity and ferroelectricity that are of potential technological interest [5]. The cross correlation between magnetism and ferroelectricity in materials with coexistence of spontaneous magnetization and polarization, termed multiferroics, has recently become a subject of great scientific impact.

Vanadium sesquioxide, V_2O_3, considered as a Mott-Hubbard metal-insulator [6] system, has been the object of intense study from both theoretical [7, 8, 9, 10] and experimental [11, 12, 13, 14] points of view in the last decades. This compound has an interesting phase diagram, with an antiferromagnetic insulator phase (AFI) at low temperatures, and a paramagnetic metallic one (PM) above the Néel temperature ($T_N \approx 150$ K). The metal-insulator transition is accompanied by a strongly first-order structural phase transition in which the room-temperature corundum structure (R$\bar{3}$c) is modified to monoclinic I2/a. In 1978 Castellani, Natoli and Ranniger [7] proposed a theoretical model to explain the magnetic structure in the AFI phase from the ordering pattern of the occupation of the t_{2g} (degenerate) orbitals. This model was considered valid until 1999, when resonant x-ray diffraction (Paolasini et al. [11]), and magnetic dichroism measurements (Park et al. [13]) demonstrated that the spin of the Vanadium atoms was $S_V = 1$, whereas the model of Castellani predicted $S_V = 1/2$.

The magnetic structure is such that the I-centering cell translation is time inverting. Because of the magnetic moments being colinear in the $\mathbf{a}_m$-$\mathbf{c}_m$ plane, normal magnetic peaks are observed only at reflections $(hkl)_m$ with even h even and odd $(k+l)$. Yet, peaks have been measured at odd h, even $(h+l)$, at the resonant prepeak of Vanadium K-edge. They were initially interpreted as produced by orbital (time-even) ordering [11, 12]. However, analyses of the observations carried out by Lovesey *et al.* [10] and Tanaka [8] demonstrated that the resonant Bragg diffraction intensities are produced by the ordering of magnetic (time-odd) V multipoles. There has been controversy on the dominant resonant event producing the measured intensisties, having been proposed a parity-even E2–E2 event [10], a parity-odd E1–E2 event [8], or a combination of them [9, 15].

In this paper we present measurements at space-group forbidden Bragg reflections $(hkl)_m$ with odd h in the low temperature monoclinic phase of V_2O_3. Together with energy profiles and azimuthal dependence, we measured the polarization dependence at a fixed azimuthal point varying the incident linear polarization with a phase-plate setup. In this way, we can obtain the Stokes parameters for the secondary beam as a function of both incident and scattered linear polarization angle, without moving the crystal. This method can elucidate the presence of resonances that are very close in energy, playing on their relative phase shifts [16]. Experiments were carried out at the ID20 beamline [17] of the ESRF. A single crystal of 2.8% Cr-doped $(V_{1-x}Cr_x)_2O_3$ ($x = 0.028$) was mounted on the four-circle diffractometer with vertical scattering geometry. For the varying linear incoming polarization, a diamond phase-plate of thickness 300 μm was inserted into the incident beam. The phase plate was operated in half-wave plate mode to rotate the incident polarization into an arbitrary plane [18, 19] described by Stokes parameters $P_1 = cos(2\eta)$ and $P_2 = sin(2\eta)$, being η the angle between the incident beam electric field and the axis perpendicular to the scattering plane, i.e., $\eta = 0$ corresponds to polarization perpendicular to the scattering plane (σ polarization). The Poincaré-Stokes parameters are defined by $P_1 = (|\varepsilon_\sigma|^2 - |\varepsilon_\pi|^2)/P_0, P_2 = 2\mathrm{Re}(\varepsilon_\sigma^* \varepsilon_\pi)/P_0, P_3 = 2\mathrm{Im}(\varepsilon_\sigma^* \varepsilon_\pi)/P_0$, with $P_0 = |\varepsilon_\sigma|^2 + |\varepsilon_\pi|^2$ the total intensity, and where ε_σ and ε_π are the components of the beam polarization vector perpendicular and parallel to the scattering plane.

Fig. 1 shows the energy profiles for the $(30\bar{2})_m$ and $(10\bar{2})_m$ reflections. They contain a single resonant peak centered around 5.465 keV, as it is expected for reflections $(hkl)_m$ with odd h, in which the resonant peak from 5.47 to 5.49 keV, ascribed to an $E1 - E1$

event is forbidden [10, 11]. Energy profiles in Fig. 1 show the presence of a shoulder at E=5.4665 keV for both reflections, which opens the possibility for the existence of two lorentzians separated by approximately 2 eV contributing to the observed intensity. This energy separation can be related to crystalline electric field energy transfer. The value of 10Dq was estimated as 2.1 eV from RIXS measurements [14]. In order to elucidate the possibility of interference of different lorentzians we have performed polarization analysis measurements of the dependence of the Stokes parameters of the secondary beam with the angle of primary linear polarization η using the phase plate (Fig. 2). In the case of the $(10\bar{2})_m$ reflection we have repeated the polarization analysis measurements at 3 different energies of the incoming x-rays (Fig. 2-b). The presence of multiple lorentzians at different energies with different tensorial properties would be revealed by the appearance of circular polarization in the polarization measurements, which can be estimated from the dependence with linear incident polarization of the measured secondary Stokes parameters P_1' and P_3', and by a variation in the shape of the Stokes parameter curves when the energy of the x-rays is changed. We try a fit of the polarization data with a real Jones matrix derived from the unit-cell structure factors for the different polarizations $F_{\sigma-\sigma'}$, $F_{\pi-\sigma'}$, $F_{\sigma-\pi'}$, $F_{\pi-\pi'}$ (formulae for the outgoing Stokes parameters can be seen in ref. 20) together with a depolarization factor $(1-1/2d\sin^2\eta)$ that multiplies the linear components N_1 and N_2 of the Stokes vector of the incoming light, being d an adjustable parameter. This depolarization produced by the phase plate depends on the angle η indicating the angle of linear polarization of the incoming beam and its maximum is expected at $\eta = 90$ degrees. From the fitting to the $(30\bar{2})_m$ data we obtain the following parameters,

$$\begin{aligned} d &= 0.162 \pm 0.011 \\ F_{\pi-\pi'}/F_{\sigma-\sigma'} &= 0.8 \pm 0.3 \\ F_{\pi-\sigma'}/F_{\sigma-\sigma'} &= 0.64 \pm 0.02 \\ F_{\sigma-\pi'}/F_{\sigma-\sigma'} &= -3.01 \pm 0.05, \end{aligned} \tag{1}$$

and from the fitting to the $(10\bar{2})_m$ polarization data we obtain,

$$\begin{aligned} d &= 0.362 \pm 0.014 \\ F_{\pi-\pi'}/F_{\sigma-\sigma'} &= 0.099 \pm 0.005 \\ F_{\pi-\sigma'}/F_{\sigma-\sigma'} &= 1.20 \pm 0.01 \end{aligned}$$

$$F_{\sigma-\pi'}/F_{\sigma-\sigma'} \;=\; 0.770 \pm 0.005. \tag{2}$$

In both cases the magnitudes of the depolarization factor d is similar to that estimated from preliminary measurements with the phase plate. We obtain two different values of the depolarization d due to the fact that polarization measurements in the $(30\bar{2})_m$ and in the $(10\bar{2})_m$ reflections were performed in different experiments. The good agreement obtained in the fittings for both reflections with experimental data for a model in which we take into account the depolarization introduced by the phase plate, together with the fact that there is no significative dependence of the shape of Stokes parameters curves when the energy of the x-rays is changed in the measurements of $(10\bar{2})_m$ reflection leads us to conclude that there is no evidence of the appearance of circular polarization and that the measured intensities in both reflections are produced by single oscillators with the same tensorial character. All of this supports the validity of fitting the data with a single oscillator model [9]. In this aspect, the model that will be used to describe experimental data differs to the case of K_2CrO_4, where there is a strong evidence of the appearance of circular polarization [16, 20] and the intensities were consequently modelled in terms of different lorentzians centered at different energies for the different resonant events.

In Fig. 3 we show the azimuthal dependence of $(30\bar{2})_m$ and $(10\bar{2})_m$ reflections measured at T=100 K in the AFI phase. In order to eliminate the effect of the absorption in the azimuthal curves, data have been corrected according to the formula

$$I_{\mathrm{corr}} \;=\; I_{\mathrm{obs}}(1 + \sin\alpha_0/\sin\alpha_1),$$

where α_0 and α_1 are the incident and reflected angles of the beam with the sample. The measured azimuthal dependence of $(30\bar{2})_m$ shows a satisfactory agreement with previously published data [9], as it can be seen in Fig. 3-a.

The azimuthal dependence and polarization data collected for $(10\bar{2})_m$reflection present a good agreement with the expression for the parity-breaking event resonant x-ray scattering $F(E1-E2)$ presented in ref. 9, being possible to fit together polarization scans curves and azimuthal data. The azimuthal and polarization data for the $(30\bar{2})_m$ reflection can also be fitted to the $E1-E2$ structure factor expressions together with $(10\bar{2})_m$ data in terms of the same set of tensorial parameters, which permits us to conclude that intensities in both $(30\bar{2})_m$ and $(10\bar{2})_m$ are produced by an $E1-E2$ event. The result of the fitting is shown in

Fig. 3. The determined parameters from fitting $|F(E1-E2)|^2$ to the data are,

$$\begin{aligned}
\mathrm{Im}\langle G_1^1\rangle/\mathrm{Im}\langle G_3^3\rangle &= 0.263 \pm 0.013 \\
\langle G_0^1\rangle/\mathrm{Im}\langle G_3^3\rangle &= 3.48 \pm 0.06 \\
\mathrm{Im}\langle G_2^2\rangle/\mathrm{Im}\langle G_3^3\rangle &= -8.38 \pm 0.02 \\
\mathrm{Re}\langle G_1^2\rangle/\mathrm{Im}\langle G_3^3\rangle &= 3.908 \pm 0.013 \\
\mathrm{Re}\langle G_2^3\rangle/\mathrm{Im}\langle G_3^3\rangle &= -0.205 \pm 0.007 \\
\mathrm{Im}\langle G_1^3\rangle/\mathrm{Im}\langle G_3^3\rangle &= -3.410 \pm 0.015 \\
\langle G_0^3\rangle/\mathrm{Im}\langle G_3^3\rangle &= -4.33 \pm 0.03.
\end{aligned} \tag{3}$$

Values for $\mathrm{Im}\langle G_1^1\rangle$ and $\langle G_0^1\rangle$ are direct estimates of the orbital anapolar moment $\langle \mathbf{\Omega}\rangle$, $\mathrm{Im}\langle G_3^3\rangle$, $\mathrm{Re}\langle G_2^3\rangle$, $\mathrm{Im}\langle G_1^3\rangle$ and $\langle G_0^3\rangle$ are estimates of the moment $\langle(\mathbf{L}\otimes(\mathbf{L}\otimes\mathbf{\Omega})^2)^3\rangle$, where $\mathbf{L}$ is the operator for orbital angular momentum, and $\mathrm{Im}\langle G_2^2\rangle$ and $\mathrm{Re}\langle G_1^2\rangle$ are estimates of the moment $\langle(\mathbf{L}\otimes\mathbf{n})^2\rangle$, where $\mathbf{n}$ is the polar unit vector. Operators $\mathbf{\Omega}$ and $(\mathbf{L}\otimes(\mathbf{L}\otimes\mathbf{\Omega})^2)^3$ are true spherical tensors while $(\mathbf{L}\otimes\mathbf{n})^2$ is a pseudo-spherical-tensor. Additional information about parity-odd tensors may be found in refs. 1, 3, 21, 22. The presence of a parity-even contribution $F(E2-E2)$ to resonant x-ray scattering in this kind of reflections has been suggested [9, 10, 15] and within measured reflections its strongest contribution would appear in the reflection $(30\bar{2})_m$ as $F(E2-E2)$ is weighted by a global multiplicative factor $\sin\nu$, with $\nu = hx+ky+lz$, being x, y, z crystallographic parameters and the h, k, and l the Miller indices of the reflection [9]. However, our fitting describes data in $(30\bar{2})_m$ with great precision, which makes us conclude that parity-even $E2-E2$ contribution is absent to a good degree of approximation. From the fitted parameters, we can determine the direction of the projection in the $\mathbf{a}_m$-$\mathbf{c}_m$ monoclinic plane of the anapolar moments of the Vanadium ions, which from the quotient between $\mathrm{Im}\langle G_1^1\rangle$ and $\langle G_0^1\rangle$ is estimated as forming 4 degrees with the $(10\bar{1})_m$ reciprocal lattice vector. In Fig. 4, we show the projection in the $\mathbf{a}_m$-$\mathbf{c}_m$ plane of the anapolar moments of the eight vanadium ions in the monoclinic unit cell, together with the arrangement of magnetic moments [23] established below T_N.

In conclusion, our results demonstrate that resonant x-ray diffraction at the V K-edge for space-group forbidden Bragg reflections of the kind $(hkl)_m$ with odd h is produced by a parity-breaking E1-E2 event, being the contribution from parity-even transitions absent

to a very good degree of approximation. Polarization analysis measurements at the $(30\bar{2})_m$ and $(10\bar{2})_m$ reflections probe the fact that the intensities measured are coming with a good degree of approximation from single lorentzians. Experimental data (azimuthal variation and polarization analysis) collected at different space-group forbidden Bragg reflections are successfully accounted within our model in terms of values for the V magnetoelectric multipoles. The derived tensorial parameters include direct estimates of expectation values of the vanadium anapolar moment and other magnetoelectric moments [9]. These results solve the controversy on the origin of the resonant x-ray diffraction intensities in V_2O_3 [8, 9, 10, 15]. The derived tensorial parameters offer a test for ab-initio calculations of the electronic structure of vanadium sesquioxide that can lead to a deeper and more quantitative understanding of its electronic properties.

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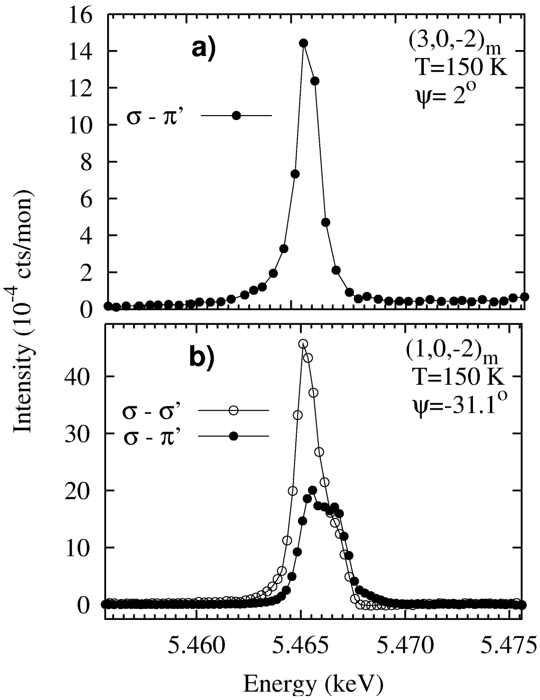

FIG. 1: Measured energy profiles of the $(30\bar{2})_m$ reflection (a) at the azimuthal angle of $\psi = 2$ degrees and $(10\bar{2})_m$ reflection (b) at $\psi = -31.1$ degrees. The origin of the azimuthal angles corresponds to $(010)_m$ reflection in the plane of scattering.

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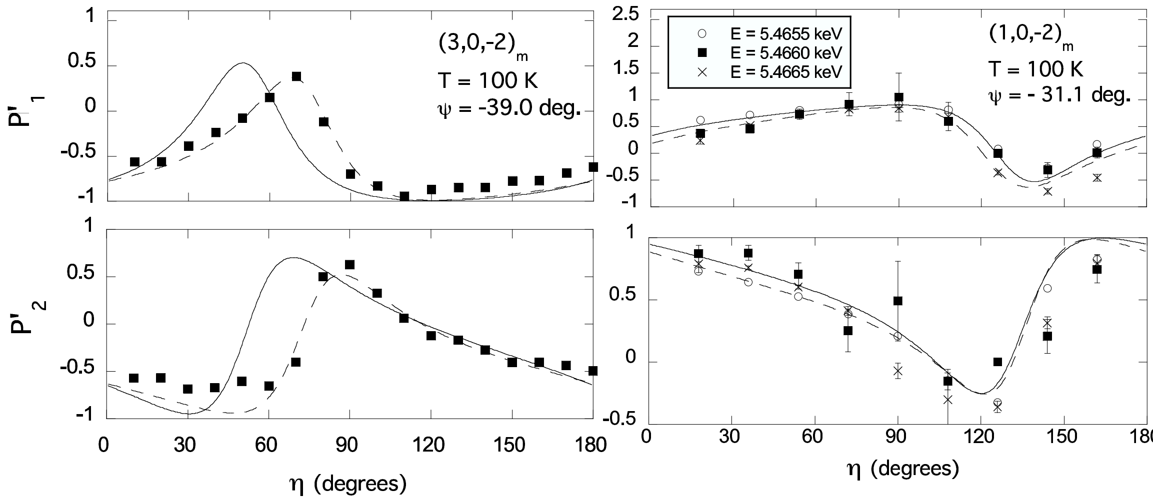

FIG. 2: Linear incident polarization dependence of the Stokes parameters P_1' and P_2' of the secondary beam in the reflections $(30\bar{2})_m$ ($\psi = -39.0$ degrees) collected at T=100 K with an incident energy of the x-rays $E = 5.4660$ keV and for the reflection $(10\bar{2})_m$ at $\psi = -31.1$ degrees and T=150 K and at three different energies $E = 5.4655$, 5.4660 and 5.4665 keV. Dashed line corresponds to the fitting of the data to a general Jones matrix produced by a single oscillator including the effect of the phase plate depolarization. Continuous line corresponds to the fitting of polarization data together with azimuthal scans using the tensorial parameters presented in eq. (3). In the origin of the azimuthal angle the $(010)_m$ reflection is in the plane of scattering.

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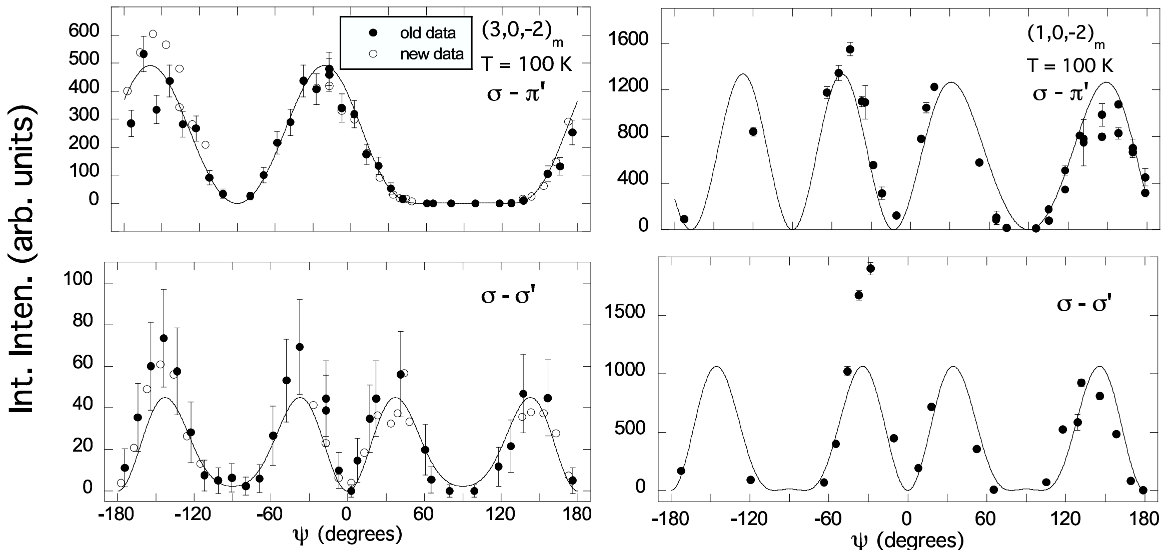

FIG. 3: Azimuthal angle scans measured on the reflections $(30\bar{2})_m$ and $(10\bar{2})_m$ at $T = 100$ K with energy $E = 5.46627$ keV. In the case of $(30\bar{2})_m$ we show the agreement of new data with previously published data [9]. The continuous line correspond to the fitting to the expressions for the $F(E1 - E2)$ scattering length presented in [9] with the tensorial parameters shown in eq. (3). At the origin of the azimuthal angle $(010)_m$ reflection is in the plane of scattering. Both polarization channels $\sigma - \sigma'$ and $\sigma - \sigma'$ are shown.

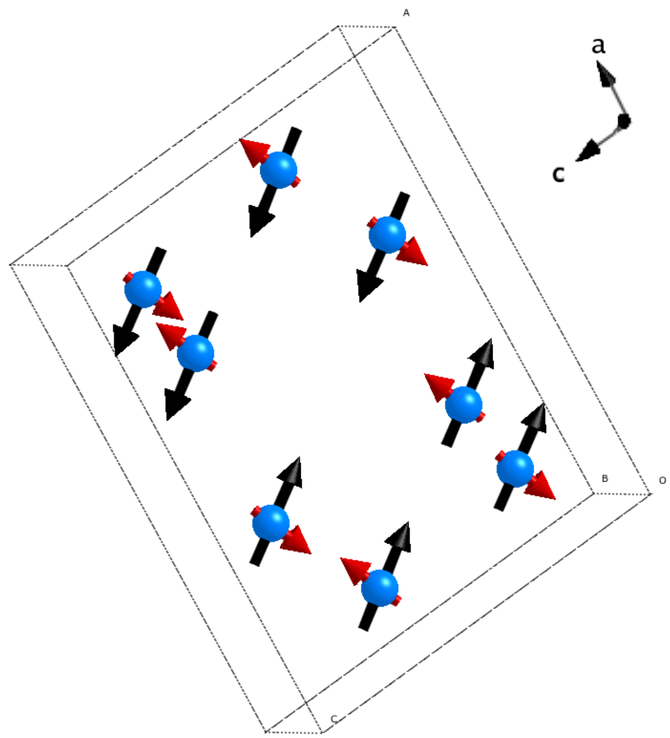

FIG. 4: (color online) Positions of the Vanadium ions in the monoclinic unit cell adopted by V_2O_3 below the Neel temperature, together with the configuration of the magnetic moments [23] (red arrows) and the determined projection of their anapolar moments (black arrows) in the $\mathbf{a}_m$-$\mathbf{c}_m$ plane. The basis vector $\mathbf{b}_m$ is normal to the plane of the diagram.